Evaluation of monomer reactivity ratios of more complex copolymerization schemes, with application to the penultimate unit effect in methyl acrylate-butadiene copolymerization

Evaluation of Monomer Reactivity Ratios of More Complex Copolymerization Schemes, with Application to the Penultimate Unit Effect in Methyl Acrylate–Butadiene Copolymerization

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Synopsis

A generally applicable computational procedure, which permits the accurate evaluation of the kinetic parameters of intricate and extended copolymerization schemes to be made, is described. This method is based on a numerical integration of the differential equation, and, according to the (improved) curve-fitting I procedure, experimental errors in both measured variables are considered. Furthermore, a description is given of the F test, in which a statistical comparison between the resulting residual sums of squares of two different schemes offers a possibility of selecting the most probable kinetic scheme for a given copolymerization system. The capability and applicability of the methods developed is demonstrated for the free radical copolymerization kinetics of methyl acrylate (MA) (M_1) and butadiene (BD) (M_2) with toluene as solvent. Here, the simple copolymer equation is unsatisfactory because a significant penultimate unit effect in BD macroradical reactivity shows up: $k_{222}/k_{221} = 0.84$, $k_{122}/k_{121} = 0.53$, and $k_{11}/k_{12} = 0.088$. The microstructure of the copolymer samples, determined by infrared (IR) spectroscopy, shows a decreasing fraction of BD units in the vinyl configuration in favor of the fraction of BD units in the *cis*-vinylene and *trans*-vinylene configuration at increasing MA (m) content. Statistical considerations indicate a strongly diminished probability of finding BD (b) in the vinyl configuration in $\sim mb \sim$ transitions. Steric hindrance or polar repulsion of the ester side group of the penultimate MA unit probably account for the increased preference for monomer addition to the C_4 site over the C_2 site of the BD macroradical.

INTRODUCTION

The kinetics of the free radical copolymerization of butadiene and methyl acrylate has not been investigated thoroughly. Walling and Davison[1] have reported on the emulsion copolymerization of this binary combination at 5°C but the calculated r values are based on only three kinetic experiments.

Copolymerizations involving butadiene as comonomer are believed[2,3] to show kinetic behavior that possibly deviates from the well-known copolymer equation of Alfrey and Mayo[4,5] because a butadiene monomer unit shows up in the *trans*-vinylene, *cis*-vinylene, and vinyl configurations in the (co)polymer chains.[6] Nevertheless, all butadiene copolymerizations reported to date were presumed[7] to obey the simple copolymer equation except for one case, namely, the acrylonitrile–butadiene copolymerization reported by Vialle et al.[8] Here, a penultimate and antepenultimate unit-dependent effect on the butadiene chain end radical reactivity has been indicated. Unfortunately the physical meaning of this behavior has not been satisfactorily explained.[8,9]

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Studies of copolymerization that involve gaseous monomers by conventional techniques such as copolymer compositional analysis and the determination of the initial monomer feed composition are laborious and inaccurate. However, because a new experimental technique has been developed in our laboratory,[10,11] a method based on quantitative, on-line gas chromatographic (GLC) analysis of the monomer feed throughout copolymerization reactions, more detailed kinetic studies on copolymerizations that involve, for example, ethylene[10,12] and butadiene became possible.

Until now the kinetic parameters of extended copolymerization schemes had always been calculated by inaccurate linearization procedures.[8,13,14] In Part A of this article, an accurate and generally applicable computational procedure, based on the numerical integration of a given differential copolymer equation, is presented. Moreover, an objective criterion for the determination and comparison of the goodness of fit of different copolymerization schemes is given.

In Part B it is shown that the simple copolymer equation[4,5] is inadequate to describe the copolymerization of butadiene (BD) and methyl acrylate (MA). A scheme that considers a penultimate unit-dependent BD macroradical reactivity leads to a better description and is consistent with our findings with respect to the decreasing content of BD units in the vinyl configuration as the mole fraction MA increases.

PART A: MATHEMATICAL ASPECTS

Estimation of Monomer Reactivity Ratios in Intricate Schemes

In an earlier article[15] the general problems that concern the evaluation of monomer reactivity ratios were discussed. In addition, a new statistically reliable method of calculation, based on the simple integrated copolymer equation[5] and taking into account experimental errors in both measured variables [(improved) curve-fitting I procedure], was presented.[15]

In this article we show that the Alfrey–Mayo model[4,5] is unable to describe MA–BD copolymerization behavior. Use of more extended and consequently more complicated models, for example, the penultimate unit model,[13,14] is required. The differential form of any given copolymerization scheme can be formally written as

$$\frac{dn_1}{dn_2} = H'(q, \beta') \tag{1}$$

where dn_1/dn_2 is the ratio of the instantaneous rates of consumption of the monomers by chain propagation, $q = n_1/n_2$ is the ratio of the molar concentrations of monomers M_1 and M_2, respectively, and β' is a vector that constitutes the various monomer reactivity ratios pertaining to a particular scheme to be defined in this article.

In all known cases in which investigators used copolymerization schemes that deviated from the simple copolymer equation, the pertaining monomer reactivity ratios were calculated from linearized forms of eq. (1). Transformations of the original eq. (1), however, simultaneously lead to transformations of the original error structure of the measured variables.[16,17] This transformed error no longer has an expected value of zero and, in fact, fundamental information has been

lost. As a consequence less reliable r values will be obtained. Furthermore, a differential copolymer equation [eq. (1)] requires a constant composition of the relevant monomer feed. Most copolymerizations will inevitably show a drift in the monomer feed ratio (q) as the degree of conversion to copolymer increases. Therefore for reliable calculation procedures of r values the integrated form of eq. (1) is preferred to the differential equation. Integration of eq. (1) will form a relationship between the changing molar feed ratio, $q = n_1/n_2$, and the degree of conversion based on monomer M_2, $f_2 = 100(1 - n_2/n_{20})\%$, where n_1 and n_2 denote the numbers of moles of monomer M_1 and M_2, successively, and the subscript zero indicates initial conditions.

Equation (1) can be rearranged to

$$\frac{df_2}{100 - f_2} = T(q, \beta')\, dq \tag{2}$$

where $T(q, \beta') = 1/[q - H'(q, \beta')]$. Integration of eq. (2) yields

$$f_2 = 100 \cdot \left\{1 - \exp\left[-\int_{u=q_0}^{u=q} T(u, \beta')du\right]\right\} \tag{3}$$

where f_{20} is set equal to zero. In the simple Alfrey–Mayo scheme the integral in eq. (3) can be evaluated analytically.[2,10,15,16] When more extended schemes are involved, however, the integral has to be evaluated numerically; for example, by the Simpson rule, described by Davis and Rabinowitz.[18] In either case the estimation of β' (= reactivity ratios) and q_0 (= initial molar feed ratio of each run) proceeds according to the procedure described[15] for the analytically integrated copolymer equation [cf. eqs. (2) and (13) in ref. 15], which accounts for an error structure, assumed to describe the accuracies and dependency in the measurements of F_2 and Q of the unknown "true" values of f_2 and q. This error structure is estimated by a careful consideration of the relationship between the errors in F_2 and Q on the one hand and the errors in the three peak areas that result from sequential gas chromatographic analysis of the copolymerizing mixture on the other.[15] Because the reaction mixture is sampled directly, measurement errors for different samples can be safely considered statistically independent. Therefore, the pair (Q_i, F_{2i}) and the pair (Q_j, F_{2j}) are independent of $i \neq j$.

As a check of the proposed calculation procedure monomer reactivity ratios were calculated by the numerical and analytical methods for the Alfrey–Mayo scheme.[4,5] Both methods led to identical results, although, as anticipated, considerably more computation time was needed for the numerical integration procedure. Computations were performed on a Burroughs 7700 computer.

Model Fitting Test

An objective test for assessing the adequacy of a copolymerization model has not yet been described in the literature.[3] In nearly all cases it has been implicitly assumed that the simple copolymer equation describes the observed copolymerization behavior. In this article, however, two methods designed to demonstrate possible deviations from the Alfrey–Mayo scheme[4,5] and assessing the goodness of fit of any particular copolymerization scheme are briefly outlined.

The first, and still slightly subjective, test is based on a comparison of the various curves in an r_2 vs. r_1 plot. Each of these almost straight lines results from a single kinetic experiment by the calculation method referred to as the curve-fitting I-intersection procedure.[15] The slope of these lines depends mainly on the average monomer feed composition during an experiment. If a drift of the intersection points as a function of the monomer feed composition is observed, it may be concluded that the simple copolymer equation is not able to describe the copolymerization behavior of the system under consideration.

A general and more objective test from a statistical point of view is based on a comparison between the residual sums of squares that result from two models, say A and B. Model B is a special case of A, meaning that B can be obtained from A by substituting known values for certain parameters or parameter combinations. To decide whether model B is appropriate the residual sums of squares that result from fitting model A, and then model B are compared. If the residual sums of squares obtained by fitting models A and B are denoted by SS_A and SS_B, respectively, p_A and p_B are the numbers of parameters to be estimated ($p_A > p_B$), and m is the number of observations, then the statistic

$$F_{\nu 2}^{\nu 1} := \frac{(SS_B - SS_A)/(p_A - p_B)}{SS_A/(m - p_A)} \tag{4}$$

provides a good approximation of the realization of an F-distributed quantity on $\nu_1 = p_A - p_B$ and $\nu_2 = m - p_A$ degrees of freedom. Critical values $F_{\nu 2}^{\nu 1}(\alpha)$ for selected probability levels α may be found in any textbook on applied statistics.[19,20] If $F_{\nu 2}^{\nu 1} > F_{\nu 2}^{\nu 1}(\alpha)$, then it may be concluded that the observed kinetic behavior is significantly better described by scheme A than by scheme B. In other words, a curve fitting by model B is significantly less adequate than a fitting by model A and as a consequence model B should be rejected. This, however, does not necessarily mean that model A is adequate.

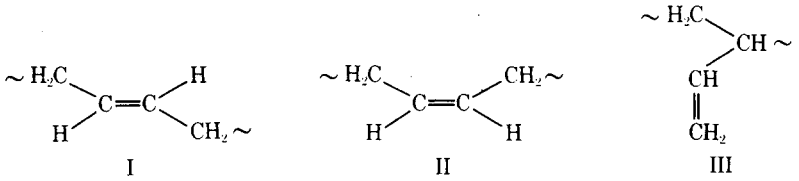
This model-fitting test provides a method of deciding, which of two alternative schemes, for instance, the Alfrey–Mayo[4,5] or the penultimate unit scheme,[13] is preferred for a given copolymerization reaction.

Furthermore, an F test offers the possibility of checking the goodness of fit of any copolymerization scheme. In this case if a particular scheme is appropriate it should describe the observed kinetic behavior more or less equally well for all monomer feed compositions with the same set of values for the kinetic parameters. A comparison is made between the residual sum of squares (SS_B) that results directly from the minimization of all m kinetic observations simultaneously for ($p_B = n + rs$) parameters and the sum $\Sigma_{j=1}^{n} SS_{Aj}$ of the residual sums of squares SS_{Aj} that results from the minimization applied to each kinetic experiment ($j = 1, \ldots, n$) separately, in which only the initial monomer feed ratio and one r value are used as unknown ($p_A = 2n$) parameters[15]; rs is the number of r values of a particular scheme. A large value of the statistic in eq. (4) leads to the rejection of the assumption that each of the $p_A - p_B = n - rs$ parameters has the same value for all n kinetic experiments.

PART B: PENULTIMATE UNIT EFFECTS IN BUTADIENE MACRORADICAL REACTIVITY IN THE METHYL ACRYLATE–BUTADIENE COPOLYMERIZATION

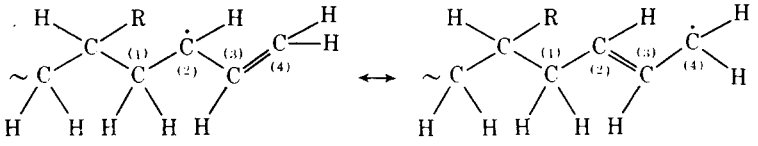
Butadiene (Co)polymerization

In (co)polymer chains formed by free radical processes, 1,3-butadiene residues appear in three possible structures; that is, the *trans*-vinylene, the *cis*-vinylene, and the vinyl configurations, as shown by structural models (I), (II), and (III):



I II III

During chain growth the BD molecule is attacked at a terminal CH_2 group by propagating macroradicals, whereas the resulting adduct radical with its odd electron is stabilized by resonance, as shown by the mesomeric structures (IV) and (V):



IV V

It must be emphasized that an adding monomer can attack at the C_2 and C_4 sites and as a consequence the configuration of the ultimate BD chain unit is being fixed at the very moment of addition of the next monomer molecule.[6,21] Although the C_2 and C_4 atoms of the allyl radical will have different reactivities toward a distinct monomer unit, it is basically infeasible to obtain the separate reactivity rate constants or monomer reactivity ratios from monomer consumption data only, as mistakenly supposed by Vialle et al.[8] In both addition reactions monomer consumption is proportional to the concentration of the BD macroradicals and the concentration of the monomers considered. Therefore it is obvious that only the sum of the rate constants of monomer addition to the C_2 and C_4 sites of a BD macroradical will be obtained. These constants can be separated only when additional information, for example, from (co)polymer microstructural investigations, becomes available.

From these considerations it follows, contrary to suppositions made by others,[2,3] that for copolymerizations involving BD the simple copolymer equation may hold in the first instance, even though the C_2 and C_4 sites of a BD macroradical exhibit different relative reactivities. Nevertheless, kinetic behavior deviating from the Alfrey–Mayo scheme may still show up, for example, when the nature of the penultimate unit affects the reactivity of one or both susceptible sites of the BD macroradical. This is the case in the present MA–BD copolymerization.

Penultimate Unit Schemes

Penultimate unit copolymerization schemes have been used in a number of cases[13,14,22] for the description of the kinetic behavior of copolymerization reactions. In these investigations reactivity ratios were calculated from a linearized form of the corresponding differential equation, which leads to unreliable r values.[16,17] Moreover, no objective criterion was used to discriminate between the goodness of fit of the different schemes.

A scheme that considers a penultimate unit-dependent radical reactivity of the BD unit ($M_2^{\cdot}$) is given by the following chain propagation steps:

$$\sim M_1^{\cdot} + M_1 \xrightarrow{k_{11}} \sim M_1^{\cdot}$$

$$\sim M_1^{\cdot} + M_2 \xrightarrow{k_{12}} \sim M_1M_2^{\cdot}$$

$$\sim M_2M_2^{\cdot} + M_2 \xrightarrow{k_{222}} \sim M_2M_2^{\cdot}$$

$$\sim M_2M_2^{\cdot} + M_1 \xrightarrow{k_{221}} \sim M_1^{\cdot}$$

$$\sim M_1M_2^{\cdot} + M_2 \xrightarrow{k_{122}} \sim M_2M_2^{\cdot}$$

$$\sim M_1M_2^{\cdot} + M_1 \xrightarrow{k_{121}} \sim M_1^{\cdot}$$

By assuming steady-state conditions for the pertaining radicals, $-d[\sim M_1^{\cdot}]/dt \simeq 0$, $-d[\sim M_2M_2^{\cdot}]/dt \simeq 0$, and $-d[\sim M_1M_2^{\cdot}]/dt \simeq 0$, an expression of the type in eq. (2) can be derived in which

$$H' = \frac{r_1 \cdot q^3 + (1 + r_2') \cdot q^2 + r_2' \cdot q}{q^2 + 2r_2' \cdot q + r_2 \cdot r_2'} \tag{5}$$

and in which q is the ratio of the molar concentrations of M_1(MA) and M_2(BD), $r_1 = k_{11}/k_{12}$, $r_2 = k_{222}/k_{221}$, and $r_2' = k_{122}/k_{121}$.

Butadiene Copolymers

In the present investigation it was found that the percentage of butadiene units in the vinyl configuration (b_2) in the MA–BD ($m - b$) copolymers decreases as the MA content increases. This can be attributed to a decrease in the occurrence of $\sim mb_2\sim$, $\sim b_2m\sim$, or $\sim mb_2m\sim$ transitions or a combination of these possibilities, compared with the probability of occurrence of b_2 units in homogeneous BD blocks (e.g., in homopolymers). The fraction (F) of b_2 in the copolymer is derived under the two most probable but slightly different sets of assumptions.

In the first derivation the special behavior of BD in $\sim mb\sim$ transitions (indistinguishable from $\sim bm\sim$ transitions in our experimental structural analysis) is assumed. Here, for any BD sequence of length j the probability of occurrence of the first BD unit (which is preceded by an MA unit) in the vinyl configuration is defined as A_1. The probability of occurrence of any of the following $(j - 1)$

BD units, including the last, in the vinyl configuration is defined as B and equals the fraction b_2 units in polybutadiene polymerized under identical conditions. The fraction of BD in the b_2 configuration in the copolymer is given by

$$F = \frac{\sum_{j=1}^{\infty} j \cdot p_j \cdot (1/j)A_1 + \sum_{j=1}^{\infty} j \cdot p_j \cdot [(j-1)/j]\, B}{\sum_{j=1}^{\infty} jp_j} = B + \frac{A_1 - B}{\sum_{j=1}^{\infty} jp_j} \tag{6}$$

where p_j is the probability of occurrence of a sequence of BD units of length j. An expression identical to eq. (6) is obtained when the probability of occurrence of a $\sim bm\sim$ transition is defined as A_1 and the probability of occurrence of any of the preceding $(j-1)$ BD units in the vinyl configuration, including the first, is defined as B.

The second expression for F is based on uncommon behavior of BD in $\sim mbm\sim$ sequences only. The probability of occurrence of a b unit, which is enclosed by two m units, in the vinyl configuration is defined as A_2. The probability of finding any other b unit in the vinyl configuration equals B. Under these constraints the fraction b_2 in the copolymer is given by

$$F = \frac{p_1 \cdot A_2 + \sum_{j=2}^{\infty} j \cdot p_j \cdot B}{\sum_{j=1}^{\infty} jp_j} \tag{7}$$

When $A_1 = B$ and $A_2 = B$, then eqs. (6) and (7), respectively, are reduced to the expression for the b_2 content of the BD homopolymer:

$$F = \frac{\sum_{j=1}^{\infty} j \cdot p_j \cdot B}{\sum_{j=1}^{\infty} jp_j} = B$$

The probability of finding a BD block enclosed by MA that contains 1, 2, or j BD units,

$$p_1 = p_{mb,m} \tag{8}$$

$$p_2 = p_{mb,b} \cdot p_{bb,m} \tag{9}$$

$$p_j = p_{mb,b} \cdot p_{bb,b}{}^{j-2} \cdot p_{bb,m}, \qquad j \geq 2 \tag{10}$$

should be known in order to test the models given by eqs. (6) and (7) and to discriminate between their goodness of fit. Starting from the penultimate unit scheme [eq. (5)], the various probabilities appearing in eqs. (8)–(10) are given by

$$p_{bb,b} = \frac{r_2}{r_2 + q} = 1 - p_{bb,m}$$

$$p_{mb,b} = \frac{r_2'}{r_2' + q} = 1 - p_{mb,m}$$

The goodness of fit of eqs. (6) and (7) in regard to the microstructural observa-

tions of the present copolymers are presented and compared in a later section of this article.

Experimental

Reagents

Butadiene: The monomer butadiene (BD), at least 99% pure, (Baker) was cleansed of inhibitor by condensing the gas from the gas cylinder into a cooled (−10°C) pressure buret.

Methyl Acrylate: The monomer MA (B.D.H. Chemicals) was purified by fractional distillation. The middle fraction (bp 80–81°C and refractive index, $n_D^{20} = 1.4035$) was used.

Toluene: Chemically pure toluene (Merck) was used as solvent without further purification.

α,α'-**Azobisisobutyronitrile:** Chemically pure AIBN (Fluka) was used as initiator.

Copolymerization

Reaction Conditions: The radical copolymerization of BD and MA was studied at a temperature of 62 ± 0.2°C under a pressure of 15 ± 0.2 kg/cm^2, with toluene as solvent and AIBN as initiator. The equipment previously described[10,11] was also used in the present kinetic investigation. The monomer feed composition was determined in each copolymerization experiment by quantitative GLC analysis.

Gas–Liquid Chromatography: Samples of constant volume (approximately 3 μl) were taken at constant time intervals (13 min) by a disk valve[11] and injected into a He-carrier gas stream. The relevant gas chromatographic conditions were column temperature, 84 ± 0.2°C; column length, 4 m; stationary phase, carbowax 20*M;* and detector temperature, 135°C. The peak areas of the components of the reaction mixture were determined by electronic integration of the detector signal.

Feed Characteristics: The total initial monomer concentration of each experiment varied from 1.75 to 3.20 mole/dm^3, whereas the molar feed ratio (q) at the start varied between 0.61 and 23.7. In all experiments almost the same quantity of initiator (7.7 mmole/dm^3) was used. Additional details on the feed characteristics of the kinetic experiments are summarized in Table I. The overall rate of copolymerization was calculated by assuming that the elapsed reaction time equals 13 times the number of samples taken during a particular kinetic experiment.

Copolymer Characterization

The reaction mixture was collected in a flask that contained inhibitor (hydroquinone), and after filtration the solution was concentrated in a rotating vacuum evaporator. From this concentrate the copolymer was obtained by further evaporation of monomer and solvent under vacuum at 50°C for 2–3 days. The copolymer products were kept under nitrogen atmosphere in a cool, dark place to prevent degradation reactions.

TABLE I
Feed Characteristics of the Various Kinetic Experiments on the Copolymerization of Methyl Acrylate (M_1) and Butadiene (M_2)

Experimental code	Initial monomer feed ratio (q_0)	Final monomer ratio (q_e)	Degree of conversion based on M_2 (%)	Number of GLC observations	Total initial monomer concentration (mole/dm^3)
I	23.278	30.548	26.45	28	2.13
H	12.183	14.332	17.49	31	1.91
F	8.003	9.212	16.04	35	1.26
J	6.112	6.847	13.82	29	2.10
A	4.214	4.752	15.20	33	0.91
E	3.802	4.098	10.46	31	1.26
G	2.283	2.412	8.91	33	2.31
K	1.976	2.060	7.96	27	1.33
D	1.467	1.523	8.12	29	1.73
B	1.036	1.067	7.57	30	1.46
C	0.613	0.623	6.62	28	1.15
L	0.1403	0.1395	4.00	18	1.32

IR Spectroscopy: IR spectroscopy is a useful tool in microstructural investigations of (co)polymer chains.[23,24] In a few cases this technique has also been used in quantitative compositional analysis of copolymers.[23] The present IR study aims at revealing the content of *trans*-vinylene, *cis*-vinylene, and vinyl configurations in MA–BD copolymers of varying composition. The copolymer composition can be calculated from the GLC data according to[25]

$$F = \frac{100 \cdot (q_0 - q_e) + q_e \cdot f_2}{100 \cdot (q_0 - q_e) + (q_e + 1)f_2}$$

where F is the mole fraction of MA in the copolymer; q_0, q_e are the quotients of the numbers of moles of MA and BD in the reaction mixture at the start and end of the reaction, respectively; and f_2 is the degree of conversion of BD (M_2) in percent.

Several quantitative microstructural IR investigations of polybutadiene have been reported.[26–30] The observed absorptions at 966, 730, and 908 cm^{-1} are invariably attributed to the CH stretch vibrations of the *trans*-vinylene, *cis*-vinylene, and vinyl configurations. Unfortunately, much uncertainty remains about the numerical values of the molar absorptivities (ϵ_{tr}, ϵ_c, and ϵ_v) of the three configurations at the characteristic wavenumbers. The most appropriate choice from the molar absorptivities reported[26–30] is made in the following manner: a BD homopolymer was synthesized and purified under conditions identical to those pertaining to the present copolymerizations. IR spectra were recorded of this polybutadiene in a CS_2 solution of known concentration. The sum of the *trans*-, *cis*-vinylene, and vinyl concentrations was calculated separately for each set of molar extinction coefficients reported, by the well-known Lambert–Beer law:

$$\frac{E_i}{d} = \epsilon_{tr_i} c_{tr} + \epsilon_{c_i} c_c + \epsilon_{v_i} c_v$$

where E is the observed absorption; d is the sample thickness; c_{tr}, c_c, and c_v are

the monomer unit concentrations of the *trans*-, *cis*-vinylene, and vinyl configurations, respectively; the index i indicates successive wavenumbers; that is, 966, 730, and 908 cm^{-1}.

The molar absorptivities reported by Morero et al.[29] appeared to lead to the best value for the total observed monomer unit concentration in synthesized polybutadiene, and therefore these absorptivities are also expected to be applicable to the quantitative determination of the three BD configurations in the present copolymer samples.

IR spectra of the copolymers were recorded in a 0.1-mole/dm^3 solution in CS_2, except for samples with high MA content which appeared to be insoluble in CS_2. The total measured BD monomer unit concentrations deviated only slightly and randomly from the concentrations determined by GLC.

Spectra of the CS_2 insoluble copolymer samples were recorded from a film on a KBr pellet. In this case only the relative concentrations of the respective BD configurations in the copolymers could be determined because the sample thickness (d) cannot be measured with sufficient accuracy. One of the copolymer samples (code K in Table I) was examined according to both techniques, and this comparison led to almost identical results for the relative concentration of the vinyl configuration. The combined results are summarized in Table II. Spectra were recorded on a Hitachi IR spectrophotometer (EPI-G).

$\overline{M}$ Measurements: The number-average molecular weight ($\overline{M}_n$) of four copolymer samples was determined with a Hewlett-Packard high-speed membrane osmometer, model 501. Toluene was used as the solvent. The results are summarized in Table III.

TABLE II
IR Results Providing the Relative Content of *Trans*-Vinylene, *Cis*-Vinylene, and Vinyl Configurations Present in Methyl Acrylate–Butadiene Copolymer Samples

Experimental code	Proportions of the different configurations of butadiene (total = 100%)			Fraction methyl acrylate in sample (GLC) (mole %)
	trans-vinylene (%)	*cis*-vinylene (%)	vinyl (%)	
I[a]	68.6	25.2	6.2	75.4
H[a]	70.8	24.9	4.3	67.5
F[a]	73.4	20.0	6.6	62.6
J[a]	70.4	24.2	5.4	60.5
A	54.0	34.4	11.6	54.8
G	67.0	20.9	12.1	49.1
K[a]	56.8	31.2	12.0	50.1
K	66.7	21.6	11.7	50.1
D	59.2	27.4	13.4	45.5
B	63.3	21.7	15.0	39.7
C	62.0	22.0	16.0	32.1
L	60.0	20.0	20.0	13.8
Homopolymer	59.7	15.3	25.0	0.0

[a] Spectra recorded by polymer film on a KBr pellet.

TABLE III
Number-Average Molecular Weight ($\overline{M}_n$) and the Number-Average Degree of Polymerization ($\overline{P}_n$) of Some Methyl Acrylate–Butadiene Copolymers

Experimental code	Methyl acrylate in copolymer (mole %)	$\overline{M}_n$	$\overline{P}_n$
I	75.4	43,000	550
H	67.5	38,000	503
K	50.1	17,000	243
D	45.5	16,000	234

Results and Discussion

Copolymerization Schemes

First of all, monomer reactivity ratios of the MA (M_1)–BD (M_2) copolymerization were calculated according to the usual Alfrey–Mayo model[4,5] from 12 experiments that contained a total of 352 observations (see Table I). By the curve-fitting I procedure[15] it was found that $r_1 = 0.093$ and $r_2 = 0.72$, which indicated that both radical chain ends appear to have a lower reactivity toward their own monomer than toward the other monomer (alternation tendency). The latter values are in reasonable agreement with those reported for the emulsion polymerization[1] of the present binary combination, where $r_1 = 0.05$ and $r_2 = 0.76$ have been found.

The relations r_2 vs. r_1 calculated by the curve-fitting I-intersection procedure[15] for the separate kinetic experiments are shown in Figure 1. This plot demonstrates that the intersection points of the almost straight lines are drifting to the right as the slope decreases, which indicates that the numerical values of the monomer reactivity ratios, defined by the simple copolymer equation, are de-

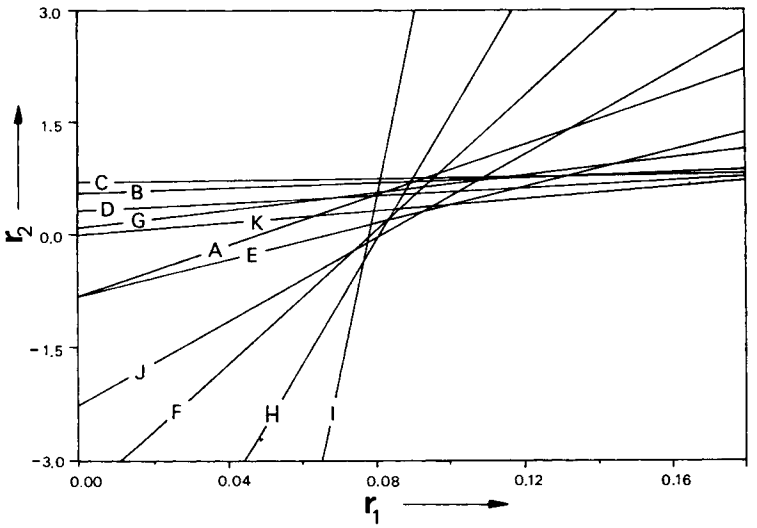


Fig. 1. Relations between r_1 and r_2 for the methyl acrylate (M_1)–butadiene (M_2) copolymerization according to the curve-fitting I-intersection procedure (experiment L coincides with experiment C).

pendent on the monomer feed composition. From these findings it may be concluded that the Alfrey–Mayo scheme[4,5] is not satisfactory for a description of the present copolymerization behavior. This conclusion has been confirmed by the more objective F test [eq. (4)], in which the residual sums of squares and the numbers of parameters pertaining to the curve-fitting I-intersection procedure [15] and the curve-fitting I procedure,[15] respectively, as given in Table IV, are compared:

$$F_{328}^{10} = [(5.129\text{–}4.672) \times 10^{-4}/(24 - 14)]/[4.672 \times 10^{-4}/(352 - 24)]$$
$$= 3.21 > F_{328}^{10}\,(\alpha = 95\%) \simeq F_{\infty}^{10}\,(\alpha = 95\%) = 1.83$$

As a consequence it can be concluded that the r_1 and r_2 values calculated from all kinetic experiments simultaneously do not fit all separate experiments equally well; thus significant kinetic information is concealed. These findings indicate unambiguously the need to extend the simple copolymerization scheme.

The calculated monomer reactivity ratios pertaining to the penultimate unit scheme [eq. (5)] are given in Table V. These data show that the r_2 and the r_2' values differ significantly from $r_2 = 0.72$, which results from the Alfrey–Mayo scheme.[4,5] This means that a BD macroradical shows a significantly lower preference for MA over its own monomer, when the penultimate unit is also a BD unit. A statistical comparison of the Alfrey–Mayo scheme (Table IV) and the penultimate scheme (Table VI) leads to the conclusion that the copolymerization behavior of the present MA–BD system is more significantly described by the penultimate scheme as

$$F_{337}^{1} = [(5.129\text{–}4.904) \times 10^{-4}/(15 - 14)]/[4.904 \times 10^{-4}/(352 - 15)]$$
$$= 15.46 > F_{337}^{1}\,(\alpha = 95\%) = 3.84$$

Moreover, the r values obtained from the present penultimate unit scheme

TABLE IV
Statistical Comparison of Two Different Calculation Procedures Based on the Simple Copolymer Equation

Calculation procedure	Number of parameters used	Degrees of freedom	Total residual sum of squares ($\times 10^4$)
Curve-fitting I-intersection	24[a]	328	4.672
Curve-fitting I	14	338	5.129

[a] Fixed value for $r_2 = 0.72$.

TABLE V
Monomer Reactivity Ratios of the Methyl Acrylate (M_1)–Butadiene (M_2) Copolymerization: Comparison of the Simple Alfrey–Mayo Scheme and the "Penultimate" Scheme[a]

Alfrey–Mayo scheme	Penultimate scheme
$r_1 = 0.093 \pm 0.003$[b]	$r_1 = 0.088 \pm 0.003$[c]
$r_2 = 0.72 \pm 0.02$[b]	$r_2 = 0.84 \pm 0.04$[c]
	$r_2' = 0.53 \pm 0.04$[c]

[a] Eq. (5).
[b] "Standard deviations," unreliable because the model is inadequate.
[c] Standard deviations.

TABLE VI
Statistical Comparison of Two Different Calculation Procedures Based on the "Penultimate" Copolymer Equation[a]

Calculation procedure	Number of parameters used	Degrees of freedom	Total residual sum of squares ($\times 10^4$)
Curve-fitting I-intersection	24[b]	328	4.668
Curve-fitting I	15	337	4.904

[a] Eq. (5).
[b] Fixed values for $r_2 = 0.84$ and $r_2' = 0.53$.

appear to have a similar significance for all kinetic experiments: $F^9_{328} = 1.84 < F^9_{328}(\alpha = 95\%) = 1.88$, which indicates that a further extension of the penultimate unit scheme [eq. (5)] cannot lead to a more significant description of the observed data. The latter assumption has been confirmed by the results from two different, more extended schemes, in which a penultimate unit-dependent radical reactivity on the MA and BD radicals, and an antepenultimate unit-dependent reactivity on the $\sim M_2M_2^{\cdot}$ radical have been considered.

Microstructural Features of the Copolymers

The microstructural features, that is, the relative concentrations of the three possible BD unit configurations, were investigated by IR spectroscopy. From the results, summarized in Table II and shown in Figure 2, it becomes possible to abstract some general and highly interesting tendencies. Figure 2 shows that the proportion of vinyl configuration in the copolymer decreases as the MA content increases. As a consequence the sum of the *cis*-vinylene and *trans*-vinylene proportions simultaneously increases. In the present discussion only the sum of the *cis*- and *trans*-vinylene configuration is considered because discrimination between these configurations is believed to be a lower-order effect that will make no significant showing.

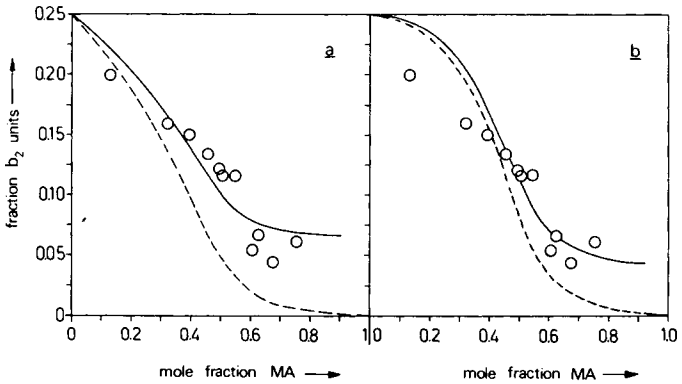


Fig. 2. Observed fraction of butadiene units in the vinyl configuration (b_2) versus the mole fraction methyl acrylate (MA) in the copolymer: (a) (- - -) all $\sim mb_2\sim$ transitions prohibited, (—) one out of 15 $\sim mb_2\sim$ transitions allowed; (b) (- - -) all $\sim mb_2m\sim$ transitions prohibited, (—) one out of 24 $\sim mb_2m\sim$ transitions allowed.

Literature on related systems provides substantial supporting evidence of the present findings. Similar results have recently been obtained by IR and NMR spectroscopy for acrylonitrile BD copolymers,[8] synthesized by the free radical method. Moreover, Foster and Binder[24] demonstrated by IR spectroscopy an analogous variation of the microstructure for six different copolymers of BD, namely, with styrene, acrylonitrile, methacrylonitrile, methyl vinyl ketone, vinyl pyridine, and α-methyl styrene, in all of which the percentage of vinyl configurations decreased as the percentage of BD in the copolymer decreased. Only the slope of the decrease was dependent on the type of comonomer. The comonomers acrylonitrile[8,24] and methacrylonitrile[24] were reported to give rise to a b_2 content approaching 0% as the fraction comonomer approaches 100%.

The present results indicate that a BD monomer unit (b) connected with a MA unit (m) has a reduced probability of occurring in the vinyl configuration (b_2), compared with a BD unit connected with a monomer unit of the same type.

A statistical approach based on eq. (6) or (7) and starting from the penultimate unit scheme [eq. (5)] offers the possibility of deciding whether the $\sim mb_2\sim$ or $\sim mb_2m\sim$ transition is hindered. The dashed curves in Figure 2(a) and (b) show the fraction BD in the vinyl configuration as a function of the mole fraction MA in the copolymer, calculated from eq. (6) for $A_1 = 0$ and $B = 0.25$ [Fig. 2(a)], and from eq. (7) for $A_2 = 0$ and $B = 0.25$ [Fig. 2(b)]; $B = 0.25$ corresponds to the b_2 content found in comparable BD homopolymers. The systematic deviations from the observed points shown by both curves indicate that a completely prohibited $\sim mb_2\sim$, as well as a completely prohibited $\sim mb_2m\sim$, transition is a too rigorous assumption. It is probable that either the $\sim mb_2\sim$ or $\sim mb_2m\sim$ transition occurs only to a limited extent.

The values of A_1 and A_2 can be obtained from eqs. (6) and (7), respectively, by minimizing the sum of squares of the differences between the observed and calculated fraction of BD units in the vinyl configuration of the copolymer. The results, $A_1 = 0.066$ and $A_2 = 0.041$, suggest that one out of every 15 $\sim mb\sim$ transitions or one out of every 24 $\sim mbm\sim$ transitions contains BD in the vinyl configuration. In polybutadiene one out of every four units is a b_2 unit.

The solid curve in Figure 2(a), according to eq. (6), provides the observed points with a somewhat better fit than does the solid curve in Figure 2(b), according to eq. (7), because the respective residual sums of squares are 4.27×10^{-3} and 5.70×10^{-3}. The curve in Figure 2(b) shows the strongest deviations from the observations at low percentages of MA in the copolymer, whereas these data, especially, constitute the most reliable observations, which indicates that a reduced number of $\sim mb_2\sim$ (or $\sim b_2m\sim$) transitions is more likely than a decreased probability of occurrence of $\sim mb_2m\sim$ transitions.

Translated into kinetic terms, a partly prohibited $\sim b_2m\sim$ transition would mean that the MA monomer unit adds to the C_4 radical site at a higher relative rate than to the C_2 radical site. This fact, by itself, definitely does not imply penultimate unit-dependent BD macroradical reactivity. On the other hand, a partly prohibited $\sim mb_2\sim$ transition indicates that the preceding MA unit affects the difference between the reactivities of the C_2 and C_4 sites of the BD macroradical. In this case penultimate unit-dependent BD macroradical reactivity will show up, provided the ratios of the BD and MA monomer addition rate constants with respect to the C_2 and the C_4 sites of a BD macroradical differ sufficiently. This appears to be the case in the present system, as shown in Table

V. The experimentally determined values $r_2 = 0.84$ and $r_2' = 0.53$ now indicate a higher ratio of the rate constants of the MA and BD addition to the C_4 site, compared with the C_2 site of the BD macroradical.

Finally, it may be concluded that a penultimate MA unit causes increased overall reactivity of the C_4 site in relation to the C_2 site of a BD macroradical, which may be explained in terms of the dipolar MA carbonyl group which causes the radical to be localized preferentially in the 4-position of the BD macroradical.

In addition, a higher preference for MA over BD addition to the C_4 site, compared with the C_2 site of a BD macroradical, is observed. Because polar effects of the penultimate unit are causing a shift in the overall C_4/C_2 reactivity of BD macroradicals, they are also expected to contribute to the MA/BD preference for addition to the respective BD radical sites.

Overall Rate of Copolymerization

The overall reaction rate (R_p) of the present MA–BD copolymerization in toluene increases with increasing BD content in the monomer feed; for example, by going from kinetic experiment I to C (see Table I) an increase by a factor of about 2 is observed.

On the other hand, the number-average degree of polymerization appears to decrease with increasing BD content in the copolymer, as shown in Table III. The contradictory tendencies of R_p and $\overline{P}_n$ (both $\sim \bar{k}_p/\bar{k}_t^{1/2}$) may be explained in terms of an increased chain transfer to solvent (toluene) with an increasing BD content in the monomer feed, whereas the subsequent reinitiation reaction is not noticeably retarded.

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